SPACE CHARGE IN LIQUID DIELECTRICS

By

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DISSERTATION

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VITA

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Space Charge in Liquid Dielectrics

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Studies were made of the unequal potential distribution commonly observed in insulating liquids under continuous potential difference. The potential distribution between parallel plates is measured in two insulating oils for over-all voltages between 500 and 1500 volts, and at temperatures between 20 and 60°C. This distribution is produced by an accumulation of space charge near the electrodes which accumulation, however, extends measurably into the volume of the liquid. The amount of space charge as computed from the potential distribution increases with increase of applied voltage and decreases with increase in temperature. On reversal of the applied voltage, the initial over-all conductivity is of approximately the same value as that preceding reversal. The initial current on reversal may remain constant over an appreciable interval, say from 1 to 4 sec. Following the initial constant value, the reverse current rises sharply to a maximum from 2 to 6 times the initial constant value, and at first rapidly and then slowly decreases to the same long-time values as that of the preceding opposite potential. In this condition, a reversal of the foregoing pattern of potential distribution takes place.

It is suggested that two types of ion are involved in the space charge, one of high mobility, and the other of low mobility, due to the accumulation about it of an aggregate of neutral molecules. Oscillographic studies of the variation of current on reversal offer means for approximate computations of the mobility of the ions involved. The mobility of the ions in a given liquid may take a wide range of values. As between different oils and for the same oil at different temperatures, mobilities vary inversely as the viscosity. In a low viscosity insulating oil a high value of 10^{-4} cm/sec./volt/cm has been observed at 22°C.

INTRODUCTION

IN a recent paper Whitehead and Marvin[1] have studied the nonlinear potential distribution between the two parallel plate electrodes of

[1] J. B. Whitehead and R. H. Marvin, Trans. A. I. E. E. **49**, 647 (1930).

a condenser having insulating oil as dielectric. They attribute the phenomenon to the accumulation of space charges in the volume of the oil near the electrodes. They further showed that if the voltage applied to the condenser is suddenly reversed, the reverse current passes through a pronounced maximum as the original potential pattern is built up in the opposite sense. From the dimensions of the condenser and the time required for the reversal of the potential pattern, they estimated that the mobility of the ions involved was of the order of 10^{-4} cm/sec./volt/cm. Herzfeld,[2, 3] using the Whitehead-Marvin curves and the ionization theory of gases as extended to liquids, arrives at the figure 10^{-6} for the mobility. Two different types of ion or perhaps a wide range of type are thereby suggested. Schumann,[4] since the above work, has studied analytically the current variations to be expected in the charge and discharge currents of condensers due to the motions of layers of space charge in the liquid dielectric, and concludes that the maxima of the type reported here are to be expected under certain conditions. This paper reports some further studies of the subject.

Scope of the Work

Two high-grade insulating oils were examined with special reference to (1) the distribution and the variation with time, following the initial application of voltage, of the potential gradient within the dielectric; (2) the magnitudes of the space charges involved; (3) the relation between the current and the potential variations following the abrupt reversal of applied voltage; (4) the mobilities of the ions involved, with special reference to the reverse current maximum.

Commercial insulating oils were used. Oil (A)

[2] K. F. Herzfeld, Phys. Rev. **37**, 287 (1931).
[3] K. F. Herzfeld, Phys. Rev. **34**, 791 (1929).
[4] W. O. Schumann, Arch. Elek. (27), p. 241 (1933).

was a clear, highly refined insulating oil, viscosity 0.23 poise at 25°C, average 30-minute conductivity 5×10^{-15} mhos/cm^3. Oil (B) was somewhat less highly refined, viscosity 15.0 poises at 25°C, average 30-minute conductivity 6×10^{-14} mhos/cm^3. The oils were received in sealed containers and were placed in the test cell without further treatment. Several other materials, principally waxes, were tested with reference to potential distribution only. The results on only one of these, a commercial paraffin, are reported. Its melting point was approximately 54°C, conductivity at 68°C, 2.6×10^{-11} mhos/cm^3.

The principal quantities measured were: current *vs.* time, potential *vs.* time, and distribution of potential gradient in the final steady state. The same observations were made for an abrupt reversal of voltage following a foregoing steady state. The observations were made at each of three voltages, 500, 1000, and 1500 volts, and over the temperature range 20°C to 45°C.

Experimental Method

The variation of the current over the first few seconds following the application or reversal of voltage was observed with an Einthoven[5] string galvanometer and rotating photographic film, operated in conjunction with a rapid charging, short-circuiting, discharging, and reversing switch, as described by Whitehead and Marvin.[6] The arrangement provides for a brief instant of short circuit of the condenser before the application of reverse voltage, for the removal of the geometric charge on the plates. For the values of the current at time intervals greater than one

[5] W. Einthoven, Ann. d. Physik **12**, 1054 (1903).
[6] J. B. Whitehead and R. H. Marvin, Trans. A. I. E. E. **48**, 299 (1929).

minute, a sensitive D'Arsonval galvanometer was used.

The oil to be tested was placed in a carefully cleaned open container into which were immersed a pair of parallel brass plates, each 311 sq. cm in area, and each completely surrounded in its own plane by a guard ring 3.7 cm wide. The back of each plate and the measuring electrodes were completely shielded. The insulation was equipped with guards maintaining leakage at a negligible level at all exposed points. The plate separation was variable up to a maximum of 1.90 cm.

The potential in any given plane in the oil between the electrodes was measured with a test electrode or probe. The probe potential was determined by a sensitive[1] zero method which avoided the passage of any charging current from the probe to the detecting gold leaf electroscope. The test probe was a thin metallic rectangular frame 6.3 cm^2 wound zigzag with 0.005 in. Therlo wire forming a grating of wide mesh. It was supported from a carriage moving in a slot attached to the electrode super-structure. The position of the probe was read with a micrometer screw. The test cell was surrounded by an oil bath, the temperature of which was maintained constant by means of immersed electric heaters and thermostatic control. Provision was also made for low temperature studies using carbon dioxide snow. The entire equipment including test cell and temperature bath was placed in a heat insulating container.

Results of Experiments

Potential gradient

In Figs. 1, 2, and 3, curves (a) indicate the characteristic variation with time of the potential at a given point in the oil following the first application of voltage. Plate separation 1.9 cm,

temperature 23°C, voltage 500, 1000, and 1500 volts. These curves show that at the instant of application of voltage, the potential at any point in the dielectric is that corresponding to a uni-

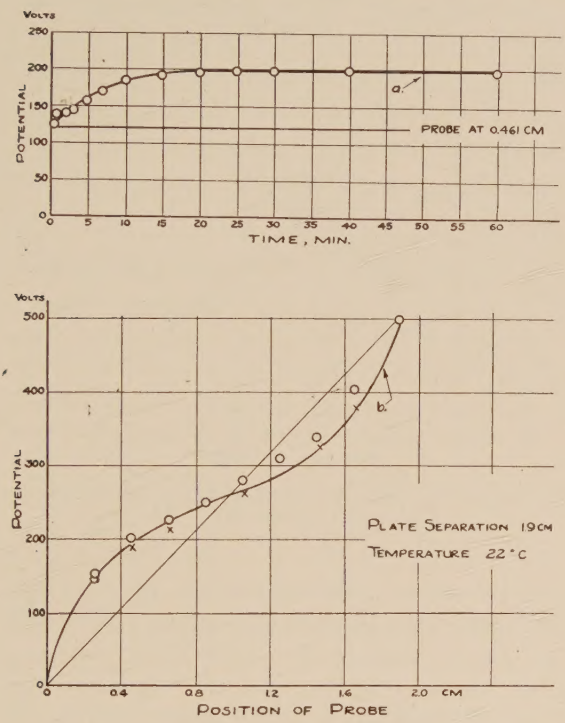

FIG. 1. Potential time curves and potential distribution for 500 volts applied to oil (A).

form gradient between electrodes. The potential then rises (or falls) rapidly from this value and arrives at a steady value only after a period of twenty minutes or more. The shape of these curves and the time intervals involved suggest an accumulation of charges of opposite sign in the neighborhood of each electrode, that the process takes place slowly, and that very sluggish ions of low mobility are involved.

Curves (b) of Figs. 1, 2, and 3 show the final potential distribution in the steady state for each

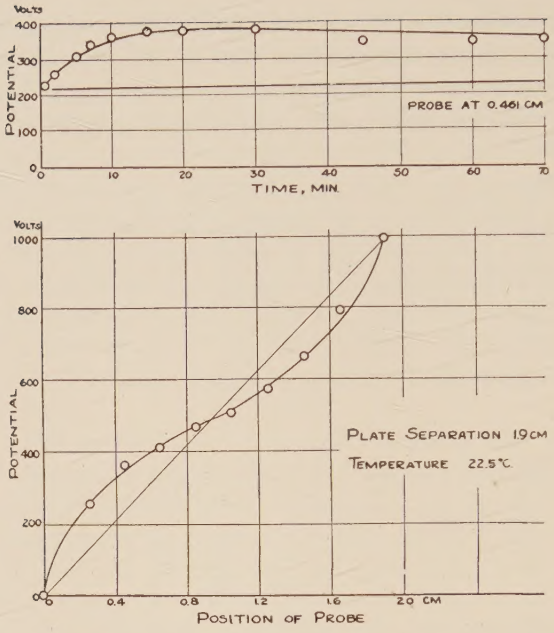

FIG. 2. Potential time curves and potential distribution for 1000 volts applied to oil (A).

of three values of applied voltage. The curves of Fig. 4 show the potential distribution for oil B. The curves indicate a symmetrical variation about the central plane with relatively high values of gradient in the neighborhood of the electrodes. This electrode gradient is greater the higher the applied voltage. Obviously the gradient at the center of the dielectric is correspondingly less than the initial uniform value. The shapes of these curves also suggest volumetrically and symmetrically distributed space charges near the electrodes and with opposite signs.

Approximate values of potential gradients may be taken directly from the curves, and may be used for a computation of the total amount of space charge accumulating on either side of the central plane.

If F_a and F_b are the measured gradients, in

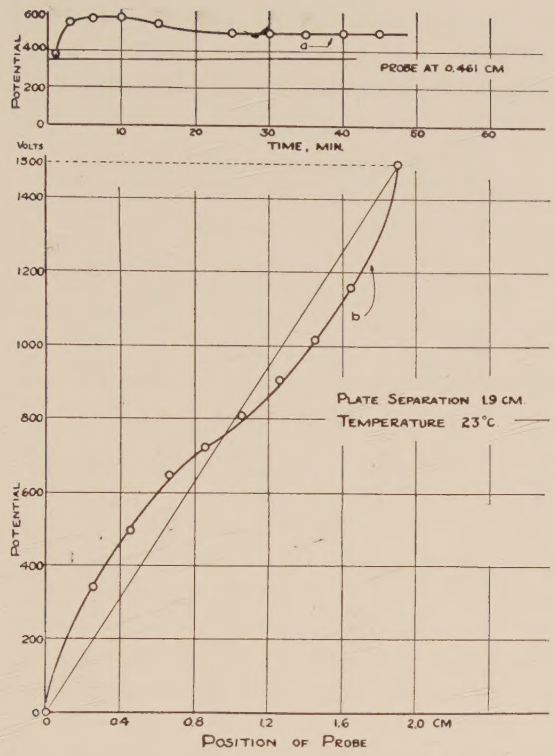

FIG. 3. Potential time curves and potential distribution for 1500 volts applied to oil (A).

electrostatic units, at one electrode, and in the center of the dielectric respectively, then by Poisson's equation, we have for the total space charge per cm² of plate area between plate and central plane of the dielectric:

$$q=\int_a^b \rho dx=\frac{K}{4\pi}(F_a-F_b) \text{ statcoulombs/sq. cm}$$

or, since F_a and F_b are measured in volts, then the charge expressed in coulombs is:

$$Q=\frac{K}{4\pi}(F_a-F^b)\left(\frac{1}{9\times 10^{11}}\right)\frac{\text{coulombs}}{\text{sq. cm of plate}}.$$

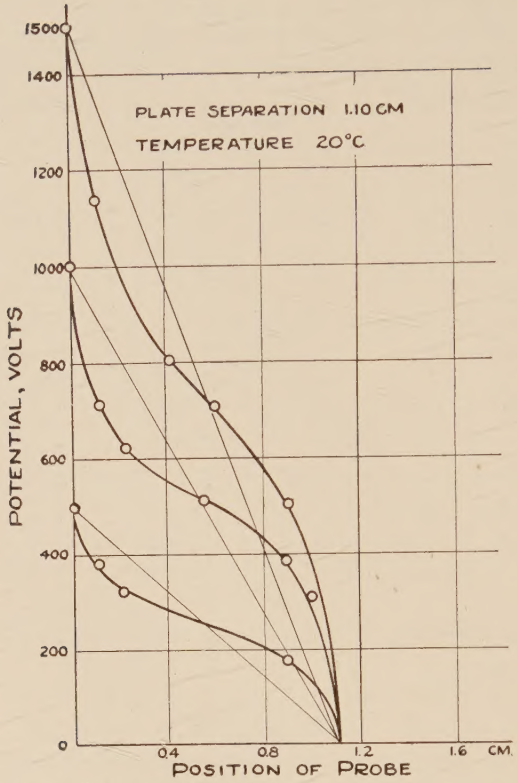

FIG. 4. Potential distribution for 500, 1000 and 1500 volts applied to oil (B).

Values as measured and computed in this way and corresponding to the data of Figs. 1, 2, and 3 are given in Table I. The values are subject to an error of ± 25 percent because of the uncertainty in the evaluation of the potential gradient. The final values of the space charge are based on the mean of the values of the gradient at the two electrodes. It is seen that the total space charge is relatively small. However, it increases with the applied voltage, and, as the over-all average gradient is relatively low in these experiments, at higher values of gradient much greater values of the space charge are to be expected.

If in the steady state of the dielectric, the applied voltage is removed, the potential of the test probe falls more or less slowly. The rate of fall is lower the higher the applied voltage and

TABLE I. *Space charge. Oils A and B.*

Specimen	Volts	Temp.	Gradient (volts/cm) Ave. F_a	F_b	Space Charge/cm² Coulombs	Stat-coulombs
			Oil (A), Plate Separation 1.9 cm			
A	500	22°C	1000	130	1.55×10^{-10}	0.465
B	1000	22.5	1420	180	2.2×10^{-10}	.662
C	1500	23	3300	380	5.1×10^{-10}	1.55
D	1500	48	2675	510	4.0×10^{-10}	1.22
			Oil (B), Plate Separation 1.1 cm			
E	500	20	2450	180	3.8×10^{-10}	1.15
F	1000	20	4450	300	7.3×10^{-10}	2.21
G	1500	20	4475	550	7×10^{-10}	2.1

the lower the temperature. The fall is more rapid if the geometric charge is removed by a brief instant of short circuit. This behavior is in general accord with the behavior indicated by the numerical data, and on the assumption that the space charges are made up of mobile ions.

If in the steady state under applied voltage, the latter is removed, the electrodes are short-circuited for a brief instant, and then connected through a sensitive galvanometer, no current is observed. In other words, there is no discharge current corresponding to the slowly decaying charging current commonly observed. This type of behavior has been frequently noted. It indicates that the accumulation of space charges near the electrodes is in large measure restrained from recombination by corresponding bound charges on the electrodes. The slow return[7] to the neutral condition through diffusion and slow recombination is by a low value conduction current in the external circuit as the opposite

[7] J. B. Whitehead and S. H. Shevki, "D–C Clean-up in Insulating Oils," presented Summer Convention, A. I. E. E., June 24–28, 1935.

space charges slowly diffuse together. These two are in opposite sense and their difference is so small as to be measured only with high sensitivity equipment.

The sign and volumetric distribution of the space charges was shown by freezing the oil while under stress, with carbon dioxide snow. The frozen oil was then removed from between the electrodes cut in half in a plane normal to the field, and each half placed, successively in a Faraday pail, giving the sign of the charge and approximate value of potential. The experiment is difficult as the oil quickly loses both solid state and stored charge. However, the results indicated clearly substantial charges in each of the halves, corresponding to the potential distribution curves of Figs. 1, 2, 3, and 4. A volumetric distribution of charge rather than a surface layer at the electrodes is thereby indicated.

The potential distribution in paraffin was also measured (see Fig. 5). The paraffin was melted into the condenser, the voltage applied while it was in the liquid state until the steady condition was reached. It was then allowed to solidify, voltage being maintained on the electrodes. After solidification, the potential distribution as shown in Fig. 5 was measured. The unsymmetrical distribution indicates that the space charge is practically entirely of one sign and suggests that the ions of one sign pass freely to the electrode whereas those of the other sign do not. Following these observations, the solid block of dielectric was removed from the condenser and tests with the Faraday pail indicated a negative charge corresponding to the location and shape of the potential distribution curve. The paraffin was also cut into two pieces in a plane parallel to the plates and the sum of the potentials observed for each half was equal to that of the whole piece before cutting. Experiments of this character must be performed

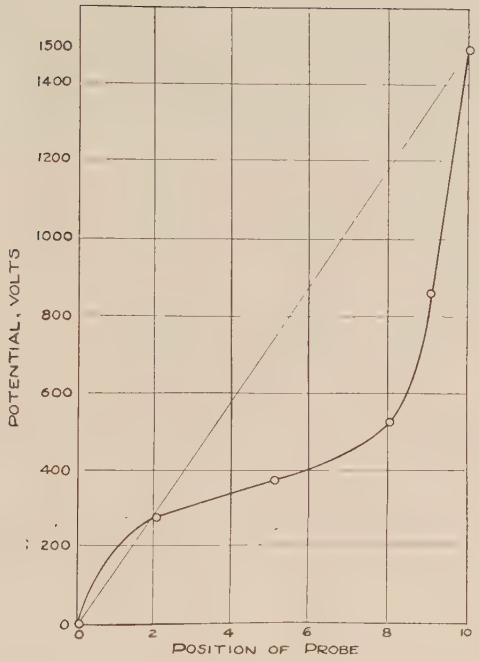

FIG. 5. Potential distribution for paraffin. 1500 volts applied.

quickly as the paraffin loses its stored charge rapidly unless carefully insulated. These observations also indicate clearly a distribution of the total space charge through the whole volume of the dielectric.

Behavior on reverse potential

If in the steady state under applied voltage, the voltage is suddenly removed, the plates short circuited for a brief instant, and then the same value of potential is applied in the opposite sense, the variation of the current with time may be followed by photographic means, using the string galvanometer or the oscillograph.[8] Photographs of the reverse current show that

[8] J. B. Whitehead, Trans. Electrochem. Soc. **65**, 83 (1934).

the current always remains constant for a few seconds after reversal, then rises quickly to a peak value and then falls away at much the same rate, or sometimes very slowly, to a final steady value. A tracing from a typical photographic exposure is shown in Fig. 6. The reverse current curves for oil (A) shown in Figs. 7 and 8 are plotted from the photographs; the upper curves show the corresponding potential variation at a selected point in the dielectric. The curves indicate that the potential on reversal passes through practically its entire variation or has arrived at its full value when the sharp maximum in the current has passed, and that it varies most rapidly while the current is passing through its most rapid variation. Numerical data taken from the curves of Figs. 7 and 8 are given in Table II. They indicate that following reversal, the current remains constant in value for a second or more. This value is usually from 1 to 2 times the value of the long time steady-state current before reversal of voltage, but never greater. The reverse current maximum is from 2 to 6 times that of the earlier steady-state current and following the sharp maximum may decrease slowly over a long time to the final steady value. The maximum increases with the potential gradient and with temperature. The reverse maximum is greatest in magnitude when observed after the space charge has reached equilibrium condition. The higher the temperature and the higher the applied voltage, the shorter the duration of the initial constant current and the sharper the current maximum on reversal. For applied voltages less than 500 volts, the reverse maximum is very low and detected only with difficulty. Values of space charge computed by integrating the area of the reverse current maximum, i.e., the area of above the long time steady (conduction) current, are

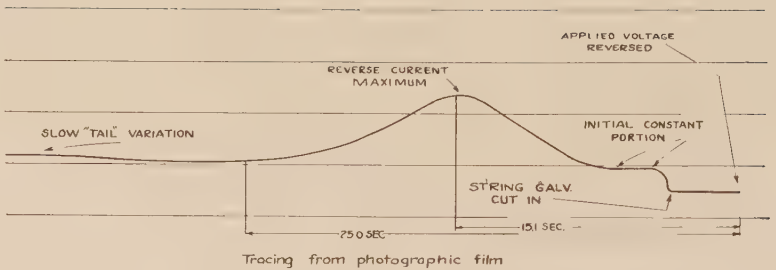

FIG. 6. Current on reversal of applied voltage. Oil (A).

TABLE II. *Ionic mobilities. Oils (A) and (B).*

SPECIMEN	VOLTS	TEMP. (°C)	CURRENT (amp. $\times 10^{-10}$) before reversal	CURRENT (amp. $\times 10^{-10}$) after reversal *initial*	CURRENT (amp. $\times 10^{-10}$) after reversal *max.*	TIME (Sec. current max.) start	TIME (Sec. current max.) crest	TOTAL SPACE CHARGE (coulombs)	MOBILITY (cm/sec./volts/cm)
				Oil (A), Plate Separation 1.9 cm					
B	1000	22.5	4.9	5.0	20	14.0	31.0	6.8×10^{-8}	1.06×10^{-4}
C	1500	23	7.0	9.0	30	4.5	15.0	15.8×10^{-8}	1.04×10^{-4}
B′	1000	44	10.0	11.5	23	2.6	11.0	5.2×10^{-8}	2.15×10^{-4}
C′	1500	47	13.0	12.5	45	1.1	6.1	11.7×10^{-8}	2.4×10^{-4}
				Oil (B), Plate Separation 1.1 cm					
H	1500	58	102.0	106.0	189.0	35	600	20.7×10^{-8}	2.1×10^{-6}
H′	1500	58	96.5	63.0	130.0	40	600	19.5×10^{-8}	2.1×10^{-6}

of the same order of magnitude as those computed from the potential distribution.

Computation of ionic mobility

The potential distribution curves reverse themselves accurately on reversal of applied voltage. The time required for such reversal is clearly indicated by the reverse current and potential time curves of Figs. 7 and 8. Knowing the distance between electrodes, and assuming that the new potential distribution on reversal is caused by the passage of the space charges to the opposite electrodes, we have a simple overall means of determining the average mobility of the ions making up the space charges. Accordingly we have: $k = d/E \cdot t$, in which k = mobility in cm/sec./volt/cm, E = gradient in volts/cm, d = average length of path of ions in cm, t = time in sec. for reversal.

In applying this formula, the most uncertain factor is t for in some cases the approach to the final steady value after reversal is very slow; however, the steep slopes of the current maxima indicate that the greater part of the space charge must change position more or less rapidly. A more accurate determination appears probable in using for the elapsed time, the interval between the initial rise of the current maximum and the maximum itself, and assuming that at the latter instant the space charges have traversed half the distance between the plates. Values of mobility so computed are given in Table II. It is seen that within the range measured, they are independent of the potential gradient, increase with temperature, and are roughly 100 times greater in oil (A) than in oil (B), corresponding to the large difference in viscosity of the two oils. It is to be noted also that the order of magnitude of the mobility in oil (A) is 10^{-4} cm/sec./volt/cm, corresponding to the earlier measurements of Whitehead and

Marvin. It may also be noted that at the maximum of reverse current, the reverse potential distribution has been largely established. This means that at this time a portion of the oil at least is subjected to the counter-gradient of the polarization caused by the space charge. This means that the resultant gradient is less than that corresponding to the applied potential and the average mobilities computed above may have somewhat higher values.

The mobility may also be computed from the value of the reverse current maximum and the total volume of space charge, again assuming that in reversal the total space charge reverses its position. Two values of the space charge are available, one as taken from the potential distribution curves and the other by integrating the area which lies above the steady state (conduction) current. The two values of space charge so computed are of the same order of magnitude, but do not agree closely. The mobilities so computed for oil (A) are about one-tenth the values computed by the first method and as given in Table II. A possible explanation is the recombination of the ions of opposite sign, as the two space charges must pass each other in moving to the opposite plates.

Discussion

Two features of the foregoing observations stand out as not being in accord with present theories of conduction in liquid dielectrics. They are: (1) the reverse current maximum, and (2) the initial relatively low constant value of current on reversal.

When in the steady state, the current voltage relations in a pure insulating liquid are very similar to those in gases, namely, initial linear relation, followed by saturation, and then rapidly rising current due to secondary ionization.

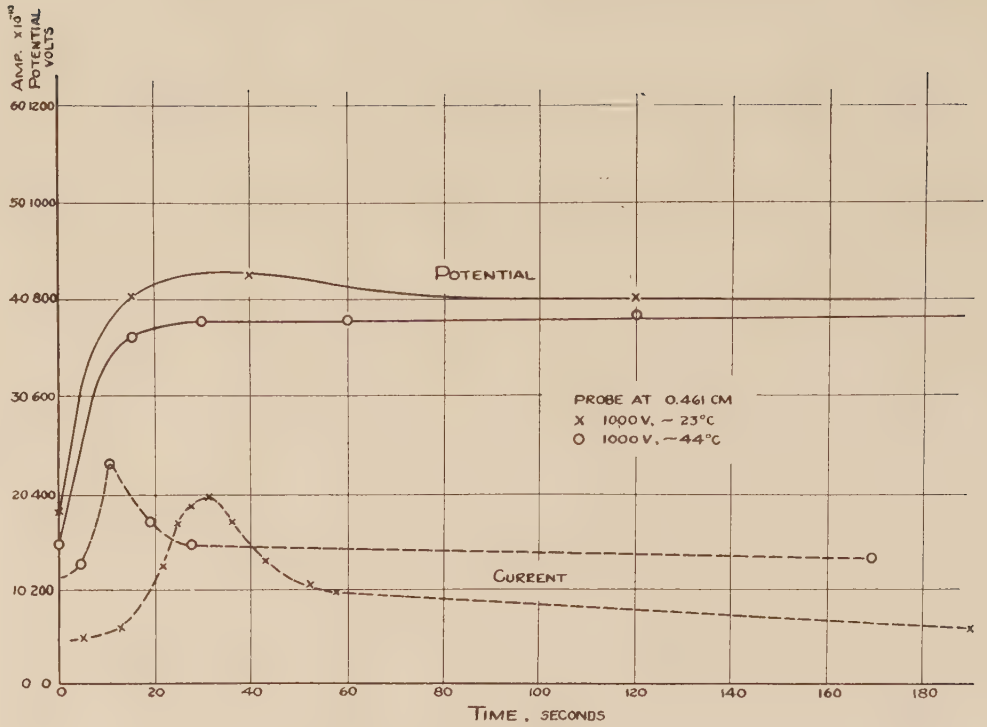

FIG. 7. Variation of potential and current on reversal at 1000 volts.

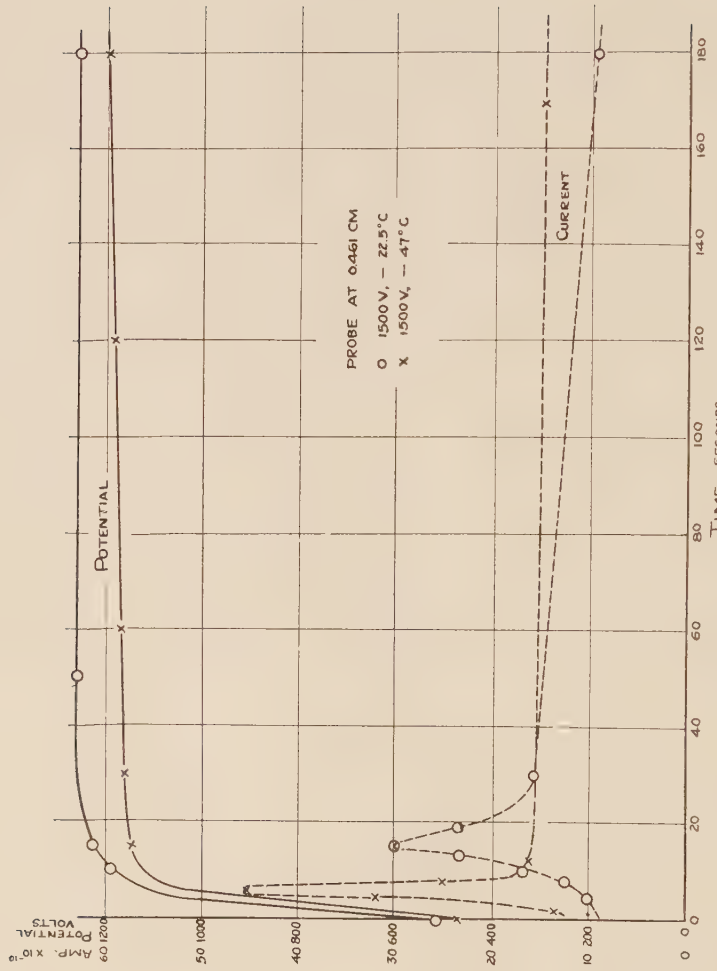

FIG. 8. Variation of potential and current on reversal at 1500 volts.

These and other relations indicate strongly that it should be possible to extend the ionization theory as developed for gases also to the phenomena of liquids.[9] Unequal potential distribution and space charges are found in gases and are in accord with gas theory. The space charges are due to space variations in ionic density, but the ions themselves are in uniform motion towards the electrodes. When the applied voltage on parallel plates is reversed, the current after reversal, in accordance with gas theory, should be approximately of the same value as before reversal, and should not vary with time. Consequently, the pronounced maxima found in the reverse current behavior of insulating liquids is apparently not accounted for by the laws explaining space charge and current in gases. The initial constant current on reversal is apparently in accord with the behavior to be expected from gas-laws. Its order of magnitude is the same as the preceding long-time steady state current. Usually it is slightly greater, and this is readily explained by the fact that immediately after reversal, the space charge polarization and the applied voltage are now both in the same direction so that the over-all gradient at the beginning of reversal is somewhat higher than that corresponding to the applied voltage. On the other hand, this initial current, although constant over an appreciable interval, then merges into the rapidly rising reverse current maximum and there appears no obvious reason why the two should be separated in seeking for an explanation.

In the neutral state, even when highly purified, insulating liquids always show some conductivity albeit of very low value, due to traces of impurities, radioactive influence, etc. The total number of ions present rises to equilibrium conditions as related to recombination and diffusion.

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[9] G. Mie, Ann. d. Physik **26**, 597 (1908).

Some of the free ions attract to themselves clouds of neutral molecules, thus constituting large and sluggish ions. Under normal electric gradients, an ion may carry with it as it moves a part of this surrounding cloud. As the gradient increases, however, it may be expected finally to shed the cloud completely.

When a potential difference is applied, if not too high, there will be motion of both the old heavy ions and newly generated free ions towards the two electrodes. The old heavy ions will move much more slowly and if they are sufficient in number a practically steady initial value of current may result as often observed.[8, 10] As the ions arrive at the electrodes, some of them are discharged, but others of them are not discharged, retaining enough of their neutral envelopes to prevent complete arrival at the electrode surface. Space charges will, therefore, accumulate near the electrodes due partly to the steady withdrawal of freshly formed ions from the central regions in accordance with gas behavior, and also due to the accumulated and more or less stationary heavy ions with their surrounding clouds of neutral molecules. As the space charge increases and the internal gradient decreases, there is a greater and greater tendency for an increase in the number of these heavy ions with relatively wide distribution through the volume of the liquid. Both of these elements of space charge are necessary for a complete explanation of the phenomena as observed.

The long-time steady state current is due principally to the constant supply of newly formed more mobile ions. The initial reverse current is due only to the newly generated mobile ions, the conductivity for this brief period being the same as the final conductivity of

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[10] J. B. Whitehead, Trans. A. I. E. E. **50**, 692 (1931).

the preceding opposite period. The reverse current maximum is apparently due principally to the space charge stored up in the large sluggish ions, consisting of molecular aggregates. No such maximum is to be expected from the new more mobile ions. A difficulty in this view exists, however, in the time interval which elapses before the rise to the maximum begins. Considered merely as mobile ions, we would expect them to take up their new direction and velocity immediately on reversal of the field. A possible explanation suggests itself as follows: The heavy ions with their envelopes of neutral ions pack more or less tightly in the region nearest the electrodes. Because of their size, the mobilities of these aggregates must be very low at the start, adding practically nothing to the conduction current. However, under the continued action of the field, particularly in the central region where the density of the heavy ions is less, and under the added influence of the counter-polarization, the ions, as they get into motion, begin to shed their neutral envelopes, thereby assuming a steadily increasing velocity. This process communicates itself in turn to the aggregates lying nearer the plates until finally the whole volume of heavy ions have shed their neutral molecules and assume their maximum possible mobility, thus setting up the reverse current maximum as observed. The accumulation of the opposite space charge then causes a decrease in velocity and a further accumulation of neutral envelopes and a return to the heavy sluggish state.

In connection with the value 10^{-4} cm/sec./volt/cm for the mobility in oil (A), it is to be noted that this figure is of the order of that corresponding to the mobilities of ions in electrolytic solutions. This is in accord with theoretical

discussions by Gemant,[11] Nikuradse,[12] and others who ascribe an electrolytic character to the conductivity of insulating liquids. Nikuradse in fact has mentioned even higher mobilities of the order 10^{-3} for certain insulating liquids. Hofmann,[13] using an optical method and cinema camera, has shown recently that the mobility of the ions in a transformer oil immediately following the first application of voltage is of the order 10^{-4} cm/sec./volt/cm. All these figures strongly suggest that the ions involved in the conductivity of insulating liquids in certain cases at least are electrolytic in their origin. However, it is to be noted that for the oils reported in this paper, as well as the others referred to, all have substantially higher values of viscosity than those for the usual electrolytic solutions, which would call for a lower mobility if the ion is of simple electrolytic character. It appears probable therefore that in the case of insulating liquids, other elements may be present than those included in the common theory of electrolytic dissociation and conduction.

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[11] A. Gemant, *Elektrophysik die Isolierstoffe* (Julius Springer, Berlin, 1930).

[12] A. Nikuradse, *Das flüssige Dielektrikum* (J. Springer, Berlin).

[13] R. Hofmann, Zeits. f. Physik **92**, 739 (1934).

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